THESIS

THE DISPERSION OF THE VELOCITY OF SOUND IN METHYL AND ETHYL ACETATE

NEIL LEWIS ELLIS, JR.

1949

THE DISPERSION OF THE VELOCITY OF SOUND IN METHYL AND ETHYL ACETATE

A THESIS

Presented to the Faculty of the Graduate School of Cornell University for the Degree of

MASTER OF SCIENCE IN ENGINEERING

By

Neil Lewis Ellis, Jr.

September, 1949

BIOGRAPHICAL SKETCH

The author was born in Fresno, California on December 8, 1920. After attending the public schools in that city, he graduated from Fresno High School in June, 1938. He attended the University of California at Berkeley, California, where he majored in Chemistry and was awarded the degree of Bachelor of Science in May, 1942. Upon graduation from the University, he was commissioned an ensign in the U. S. Naval Reserve, serving in the Pacific Theater during World War II. In July, 1946 the author was commissioned a Lieutenant in the U. S. Navy and commenced the Naval Postgraduate Course in Ordnance Engineering, Chemical, at Annapolis, Maryland. In September, 1947 he was detailed to Cornell University to complete this course and since that time has been enrolled in the Graduate School of Cornell University.

ACKNOWLEDGMENTS

The author would like to express his appreciation to Dr. H. J. Cook for suggesting the topic of the investigation and for his invaluable suggestions and guidance during the progress of the work. He would like also to express his thanks to the U. S. Navy Bureau of Ordnance for providing the opportunity and the financial support of his studies and also to the Office of Naval Research for partial support in setting up the equipment.

TABLE OF CONTENTS

I. INTRODUCTION AND THEORY

It was the aim of this work to investigate the variations of the sound velocity with frequency in the ultrasonic range (two to five megacycles) in certain organic liquids which show abnormal sound absorption properties in that frequency region. In the past it has been possible to use the properties of sound velocity and absorption to make theoretical conclusions concerning the molecular and atomic structures of certain gases and liquids. It was anticipated that the investigation described in this paper would provide further information concerning the liquid structure of the compounds under examination, namely, the acetates.

The most successful correlation between theory and experimental work with ultrasonics has been made in the field of gases. In isotropic and homogeneous media, assuming that the sound vibrations take place adiabatically, the velocity of a sound wave is given by:

$$V = \sqrt{\frac{\gamma}{\rho \beta_{iso}}} = \sqrt{\frac{1}{\rho \beta_{adia}}}$$

where V is the velocity, γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume, ρ is the density, and β is the compressibility, isothermal or adiabatic. In ideal gases, where Pv = constant, $\beta_{iso} = \frac{1}{P}$ since $\beta_{iso} = \frac{1}{V}\left(\frac{dV}{dP}\right)$ where P is the pressure and v is the volume. Therefore we have for the velocity:

$$V = \sqrt{\frac{P\gamma}{\rho}}$$

which is LaPlace's equation for the velocity of sound in gases.

With regard to the absorption of sound in gases, the classical theory gives for a plane wave an exponential decrease in the intensity with the distance from the source. Thus we have

$$I = I_o e^{-2\alpha x}$$

where I is the intensity of the sound at a distance X from the point where the intensity is I_o, and α is the coefficient of absorption. The coefficient of absorption, according to the classical theory, is composed mainly of two parts: one due to the viscosity of the medium as described by Stokes[1] and one due to the thermal conductivity of the medium as described by Kirchhoff[2]. The resultant expression for the coefficient of absorption which varies as the square of the frequency is given by:

$$2\alpha = \frac{4\pi^2\nu^2}{V^3\rho_o}\left[\frac{4}{3}\eta + \frac{\gamma-1}{C_p}K\right]$$

where ν is the frequency, V is the velocity of sound, ρ_o is the mean density, γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume, η is the coefficient of viscosity, C_p is the specific heat at constant pressure, and K is the coefficient of thermal conduction.

In experiments with gases at accoustic frequencies, it has been found that the LaPlace equation for the sound velocity fits quite well and that the observed absorption coefficient, while it follows the variation with the square of the frequency,

$$\Gamma = \Gamma_0 \, e^{-2\alpha x}$$

$$\alpha = \frac{4\pi^2 \nu^2}{V^2 \rho} \left[\frac{\eta}{3} + \frac{\zeta}{2} \right]$$

was usually higher than the value predicted by the classical theory. However, when the frequency was moved to the ultrasonic regions, some results unexplainable by the classical theory were obtained. Pierce[3], in measuring the velocity of sound as a function of the frequency in carbon dioxide, first found that the velocity increased as the frequency was increased. Kneser[4] later showed that the velocity of sound in carbon dioxide was constant as the frequency was increased up to about 10^5 cycles/second, but that the velocity then increased slowly, reaching a value about 4% higher than initially at about 10^6 cycles/second. The sound velocity then remained constant at this higher value, with further increases in the frequency. A dispersion of the sound velocity in the ultrasonic range has since been confirmed for many polyatomic gases, while monatomic gases and hydrogen were found to show no dispersion with an increase of frequency.

In those gases which showed sound velocity dispersion, the absorption of sound was also found to be abnormal. It was usually much greater than the value predicted by classical theory. It was discovered also that the absorption was particularly strong in the frequency region in which the velocity dispersion took place, the sound absorption per cycle reaching a maximum at a frequency about midway in the velocity rise. This behavior has been shown experimentally by many observers, including Nekalepajew[5], Rich and Pielmeir[6], Grossman[7], and Abello[8].

The classical expressions for the sound velocity and the sound absorption, as given earlier, do not allow for such behavior of these properties. Any dependence of the sound velocity on the absorption as calculated from classical theory is too small to account for the observed dispersion. By using the work of Einstein[9], it was possible to explain the experimental results if the gas was an equilibrium mixture of the components of a chemical dissociation (as e.g. $2NO_2 \rightleftharpoons N_2O_4$). In such a case, at low frequencies the specific heat contains the heat of dissociation, and if the specific heat is independent of frequency, there may be a time lag in the dissociation reaction. On the basis of a suggestion of Jeans[10], Herzfeld and Rice[11] gave the first theoretical explanation for velocity dispersion and anomalous absorption for non-dissociating gases, basing the explanation on a slowness of energy exchange between the translational and internal degrees of freedom of the molecule. Kneser[4] worked out the theory of such a process in detail and Rutgers[12] later made a further expansion of this treatment. Bourgin[13] made a statistical treatment of the problem based on a three-state gas (one translational state and two vibrational states, each state with a different relaxation time) and obtained a result which he later showed was equivalent to Kneser's.

A brief explanation, following the Kneser theory, of the anomalous variation of the sound velocity and absorption follows. In a polyatomic gas the molecules have three types of degrees of freedom - translational, rotational, and vibrational. Consider

such a gas at a temperature at which only a small number of the molecules are in their first excited state with regard to their vibrational energy. Suppose now that a change in the total energy occurs, such as in a sudden adiabatic compression. It is assumed that the translational part of the energy immediately follows a temperature increase and establishes the new equilibrium state without delay. The rotational part apparently follows the increase with only a very short delay. However, for vibrational energy there is a definite time lag in adjusting to the new equilibrium condition, the lag following an exponential behavior. The time constant for this vibrational adjustment is known as the relaxation time. Since the rapid compressions and expansions of a sound wave cause such temperature changes, the time lags in these energies become important considerations. When the frequency of the wave is low, each type of degree of freedom has sufficient time to complete its energy interchange. This means that the specific heat at constant volume of the gas, which is composed of contributions from all types of energy, is at its full value, and the sound velocity is at its normal low frequency value. As the sound frequency increases and approaches the reciprocal of the relaxation time, the vibrational degrees of freedom have not sufficient time to reach the equilibrium state corresponding to the temperature changes. This results in a decrease in the specific heat for the periodic process of the sound wave, till finally at frequencies much higher than the

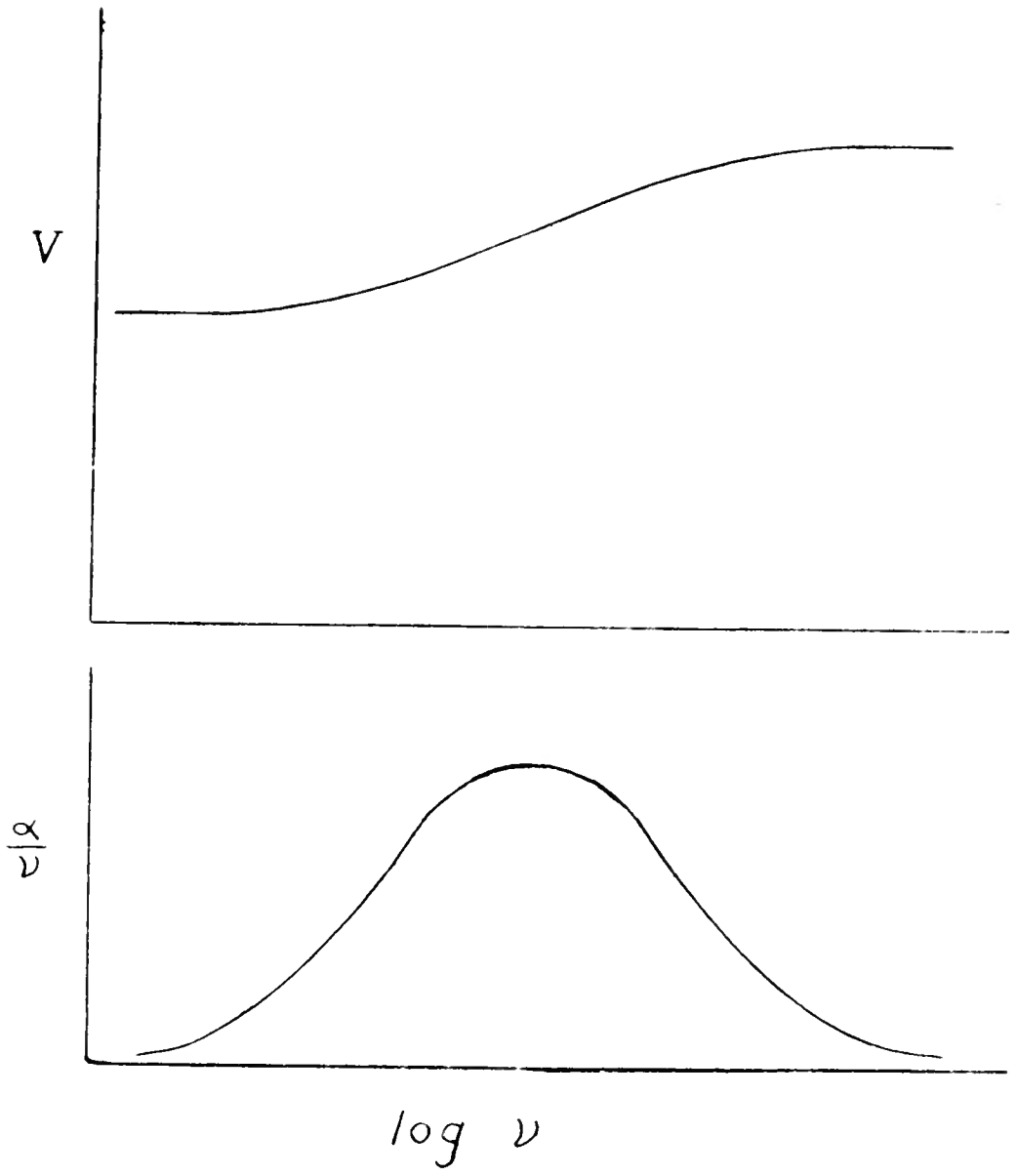
reciprocal of the relaxation time, the specific heat contains only the translational and rotational components. Consequently since γ , the specific heat ratio, increases with decreasing specific heat at constant volume, the sound velocity increases slowly as less and less of the vibrational interchange is allowed to take place, until it again becomes constant at high frequencies. The velocity now corresponds to a specific heat due to the rotational and vibrational degrees of freedom only.

Such a relaxation time process, as described in the previous paragraph, also explains the anomalous absorption reported experimentally for these gases. There is a phase difference between the pressure and volume changes in the sound wave because the time lag in the establishment of the vibrational energy equilibriums also affects the pressure. This phase difference requires that the gas do work during each cycle and part of the sound wave energy is absorbed. The absorption per cycle increases linearly with frequency at low frequencies and reaches a maximum when the frequency is equal to the reciprocal of the relaxation time. At frequencies greater than this the absorption decreases as the reciprocal of the frequency.

Thus for polyatomic gases which show dispersion, if we make a plot of the sound velocity (V) and the absorption coefficient per cycle $\left(\frac{\alpha}{\nu}\right)$ due to the dispersion process against the logarithm of the frequency, a result such as that shown in figure 1 may be expected and explained. Many other associated phenomena have been observed in gases and, in general, the Kneser theory, as it is commonly called, can well explain them.

$$\left(\frac{\partial}{\partial x}\right)$$

Figure 1



Behavior of the Sound Velocity (V) and the Absorption Coefficient per Cycle ($\frac{\alpha}{\nu}$) as the Frequency of Sound Waves is Increased in a Polyatomic Gas which shows Dispersion.

When we look at the situation in liquids, the explanation of experimental results by theory is not at all satisfactory. While not nearly as many measurements have been made in liquids as in gases, and while the agreement among those which have been made is not too good, one result is common to all the measurements dealing with the absorption. This is the fact that the absorption coefficient, as found for many polyatomic liquids, is from two to several hundred times the value predicted by the classical theory. This was first noted by Biquard[14] with a radiation pressure method and was further confirmed by Sörenson[15], Claeys Errera and Sack[16], Lucas[17], Bazulin[18], Bär[19], and many others. The behavior seems to be different for non-associated liquids and for associated liquids such as water and primary alcohols. In both cases the absorption is greater than expected; but for associated liquids the absorption coefficient has a negative temperature dependence, while for non-associated liquids the temperature dependence is positive. In some cases the absorption coefficient varies as the square of the frequency as predicted in the classical theory, while in others the coefficient seems to vary roughly as the first power of the frequency.

No satisfactory explanation has been given for this behavior. Lucas[17] showed that fluctuations in density were not sufficient to cause such results but that some sort of sub-microscopic structure in liquids might be responsible. Excessive amplitude and improper apparatus design have also been blamed, but Bär showed that these could not be the cause by obtaining the normal

classical result for mercury, a monatomic liquid. Another cause for abnormal absorption, which should be in evidence at least to some extent, might be a Kneser relaxation process such as has been described above for gases.

The use of this last theory as an explanation for the abnormal absorption brings up the point that, if true, a dispersion of velocity should result along with the anomalous absorption. To date the bulk of the experimental work aimed at finding any dispersion has located no such phenomenon. Hiedeman and his co-workers[20] have reported dispersion in several liquids, while many others, including Parthasarathy[21], Spakovskij[22], and Willard[23] did not. Richards[24] points out that for two reasons dispersion is not to be expected in ordinary liquids until very high frequencies. First, the rate of attainment of translational equilibrium is considerably greater in liquids than in gases, due to the greater numerical density, thus lowering the lifetime of the internal energy states. Secondly, the specific heats of liquids are much higher than those of gases, and the absence of the vibrational parts would be difficult to detect.

One group of liquids which seems to show consistent anomalous behavior is that containing the acetate radical. Acetic acid shows both dispersion and anomalous absorption[18,22,25] and the explanation seems to involve either the heat of dissociation or the dimer formation. Other work on the acetates by Bazulin[18], Biquard[14], Parthasarathy[27], Beyer and Smith[28], and

Bär indicates that the absorption coefficient varies approximately as the first power of frequency rather than the second with an increase of frequency.

Claeys Errera and Sack[16] obtained some very interesting absorption results with methyl and ethyl acetate, using a radiation pressure method by which they confirmed Biquard's values for several liquids. In the case of the acetates, not only were their values for the absorption coefficient much higher than the classical result, but between three and four megacycles they found an anomalous absorption region. For methyl acetate, the ratio of the absorption coefficient to the square of the frequency, $\frac{\alpha}{\nu^2}$, which by classical theory is a constant, was found to be about 1100 x 10^{-17}(seconds)^2/centimeter compared to 14 x 10^{-17}(seconds)^2/centimeter by classical theory when the frequency of the oscillations was below three megacycles. At about three megacycles this quantity took a sharp drop in value until it reached about 300 x 10^{-17}(seconds)^2/centimeter at four megacycles, and thereafter the value decreased slowly. Ethyl acetate behaved similarly but with a smaller relative drop, going from a value of about 300 x 10^{-17} (seconds)^2/centimeter at three megacycles to about 175 x 10^{-17}(seconds)^2/centimeter at four megacycles. Such behavior is in some ways similar to the anomalous absorption in polyatomic gases which has been successfully explained by the Kneser theory. One discrepancy is, however, that the change in $\frac{\alpha}{\nu^2}$ is much steeper for these liquids than would be expected from the application of the

relaxation theory. The authors, after discussing other possible causes, felt that some sort of relaxation time theory was the best hypothesis from which to start. If such a theory does apply in this case, then it might be expected that a dispersion of velocity might also be found in this region.

A search of the literature on this subject has failed to disclose any further work along this line with these liquids at this particular frequency, although some results indicate no dispersion at other frequencies. Thus, with this example of possible anomalous absorption present, an investigation was undertaken to ascertain whether a dispersion of the sound velocity could be obtained as the frequency is increased from two to five megacycles.

The amount of any velocity dispersion is almost impossible to estimate, there being several unknown factors. Pinkerton[26], in discussing the anomalous absorption of acetic acid, proposes a method for approximating from estimated absorption values the amount of expected dispersion. Using the Kneser equation for the absorption coefficient due to a relaxation time process, he states that the relative dispersion is given approximately as:

$$\frac{\Delta V}{V} \approx \frac{\alpha V}{\pi \nu_m} = \frac{\alpha V \nu_m}{\pi \nu_m^2} = A \frac{V \nu_m}{2\pi}$$

where V is the velocity, ν_m is the critical frequency of the anomalous absorption process, α is the absorption coefficient at ν_m, and $A = \frac{2\alpha}{\nu_m^2}$. From graphs of the data available for acetic acid he obtained $A = 12000 \times 10^{-17}$ (seconds)^2/centimeter,

critical $\nu_m = 2 \times 10^6$ cycles/second, and $V = 10^5$ centimeters/second. Using these values and the equation above, he obtains a relative increase in the velocity of about 0.4%. Spakovskij[22] reported a velocity dispersion of 1.0% in acetic acid, indicating that this estimate may be too small. Absorption values determined by Claeys, Errera, and Sack[16] for methyl acetate were $A = 1100 \times 10^{-17}$ (seconds)^2/centimeter and $\nu_m = 3.5 \times 10^6$ cycles/second and the velocity is about 1.2×10^5 centimeters/second. Using a calculation similar to Pinkerton's, we obtain a relative dispersion of about 0.05%. It was therefore desirable to obtain from the present experimental investigation results with a maximum error of less than 0.1%. An error greater than this would not permit definite conclusions about a dispersion of velocity as estimated above.

II. METHOD OF MEASUREMENT AND APPARATUS

In measuring the velocity of ultrasonic waves, two basic methods have been developed, one using the interferometer principle first developed by Pierce[29], and the other an optical method first put forward by Debye and Sears[30] and Lucas and Biquard[31]. Recently, a third method involving pulse techniques has proved useful. The interferometer principle has been the most popular and depends on reflecting sound waves from a reflector back to the wave generator and setting up standing waves. The wave length may then be determined from changes in the oscillator circuit current as the distance between the reflector and the generator is changed. Then, knowing the wave length and the frequency, the sound velocity may be computed. The sound wave generator is usually a quartz crystal driven by a vacuum tube oscillator. A variation of this interferometer principle is used in this experiment.

Before considering the apparatus in detail, it would be appropriate to consider the principles involved and the results that can be expected. The wave length of a sound wave is given by

$$\lambda = \frac{V}{\nu}$$

where λ is the wave length, V is the velocity, and ν is the frequency. Now if a plane wave is propagated from one plane surface toward another plane surface parallel to the first, standing waves are produced when the distance between the

$$\lambda = \frac{V}{\nu}$$

surfaces is an integral number of half waves. For a standing wave the following relation is then true:

$$\frac{\lambda}{2} = \frac{d}{n},$$

where d is the distance between the surfaces and n is the number of half waves between the surfaces. If we combine the preceding expressions, by solving each for the wave length and equating, we obtain

$$\frac{V}{\nu} = \frac{2d}{n} \qquad \text{or} \qquad \nu = \frac{V}{2d} n$$

If the velocity of sound in the medium between the planes is a constant and the distance between the planes is also kept constant, then the only quantity which will change, as the number of half waves between the planes is varied, will be the frequency. If for n_1 half waves, the frequency is ν_1 and for n_2 half waves, the frequency is ν_2, then

$$\nu_2 - \nu_1 = \frac{V}{2d}(n_2 - n_1)$$

$$\text{or} \qquad \Delta\nu = \frac{V}{2d}\Delta n$$

where $\Delta\nu = \nu_2 - \nu_1$, and $\Delta\nu$ is the frequency increment necessary to change the integral number of half waves in the standing wave pattern by the increment $\Delta n = n_2 - n_1$.

The apparatus used in these experiments was designed to utilize this principle. Two quartz crystals were placed a fixed distance apart in the liquid, and one was set into oscillation

$$\frac{\lambda}{2} = \frac{n}{d}$$

producing ultrasonic waves. The oscillations were transmitted through the liquid and received on the other crystal, setting it into oscillation. These received oscillations were transformed to electric signals, amplified, and the output current was measured. It was then possible to locate the conditions of standing waves between the crystals by changing the frequency of oscillation until the output current was at a maximum. At any frequency where a standing wave pattern was not established the output current was appreciably below this maximum.

The frequency range under investigation was from two to five megacycles and the principles described above required that the frequency of oscillations of the crystal be variable by small amounts but with the smallest possible change in the amplitude. To accomplish this, it was necessary to drive the crystal at frequencies well away from the resonant frequency — that is, the resonant frequency of the crystal was required to be well above five megacycles. In these experiments two seven megacycle crystals were used and the transmitter crystal was driven by a variable high frequency oscillator. This method of driving the crystal far from resonance gave small amplitudes of oscillation and a low efficiency of the receiver crystal, however, and thus required high amplification.

Now, if the crystal oscillates at a frequency which gives a peak in the output current from the receiver crystal, we have standing waves between the crystals. If the frequency of the oscillations is changed, the output current changes through

a series of minima and maxima, each successive maximum representing a change in the standing wave pattern by a half wave.

Using this method it is possible to check for the dispersion of velocity by making several measurements over the whole frequency range. As shown earlier, a chosen change in the number of half waves between the crystals is characterized by an increment of frequency provided that the sound velocity and the distance between the crystals remain constant. If there is no dispersion of velocity, then the small increment in frequency necessary to change the standing wave pattern by the given number of half waves will remain constant regardless of the initial frequency from which the increment is measured. If there is dispersion, then the frequency increment will change as the initial frequency approaches the region of dispersion. If the mechanism of dispersion is due to a relaxation time phenomenon, an increase in the sound velocity may be expected.

Let us now proceed to the details of the apparatus. A block diagram of the arrangement of the various units of the apparatus appears in Figure 2. The units shown are a liquid tank with the crystals inside, an oscillator connected to one crystal to give the desired frequency of oscillations, an amplifier connected to the second crystal, a square-law vacuum tube voltmeter to provide further amplification, a microammeter to measure the output current, and a device (which will be discussed later) to measure the frequency increment.

The liquid tank was rectangular in shape and was constructed

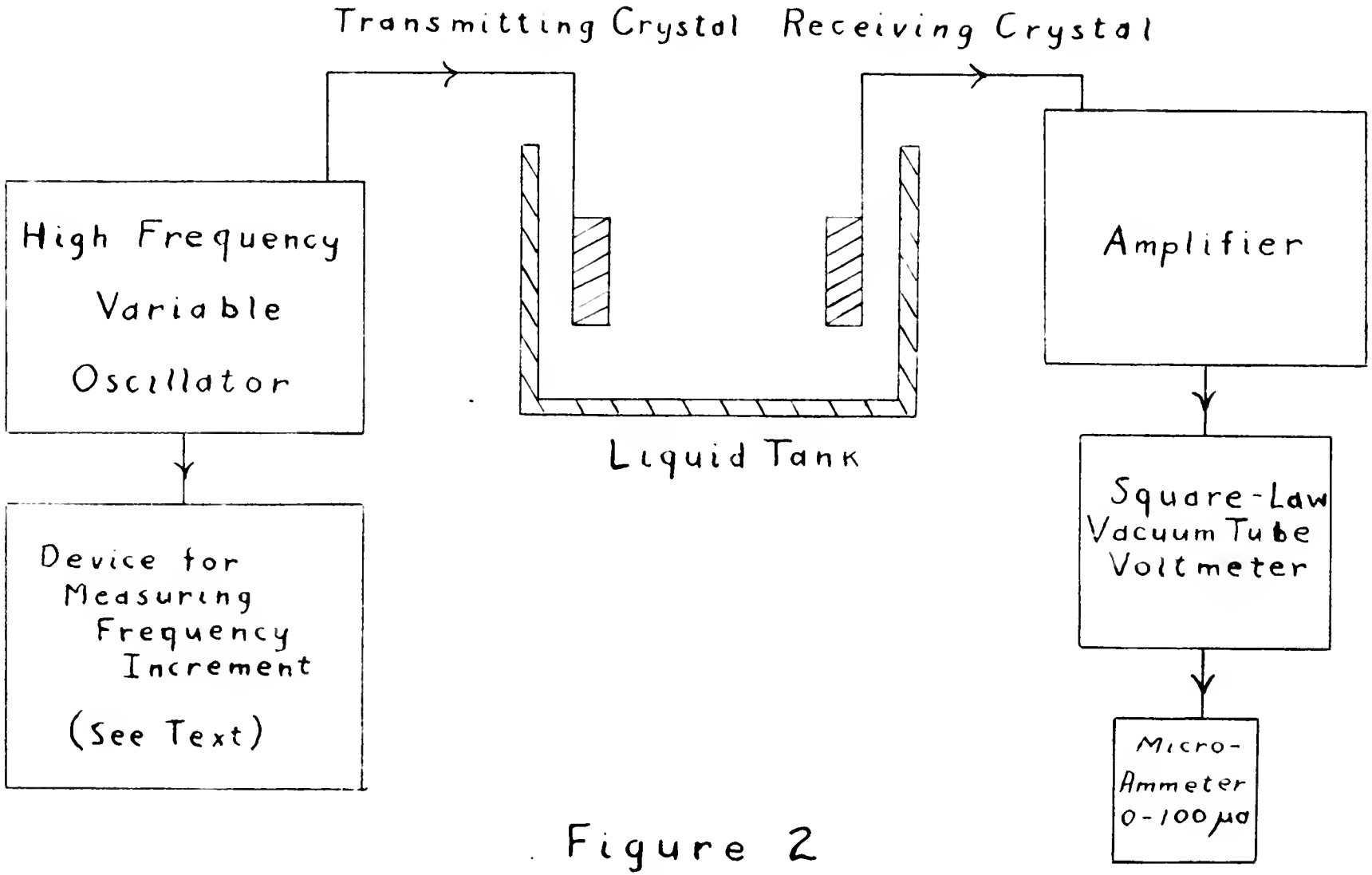


Figure 2

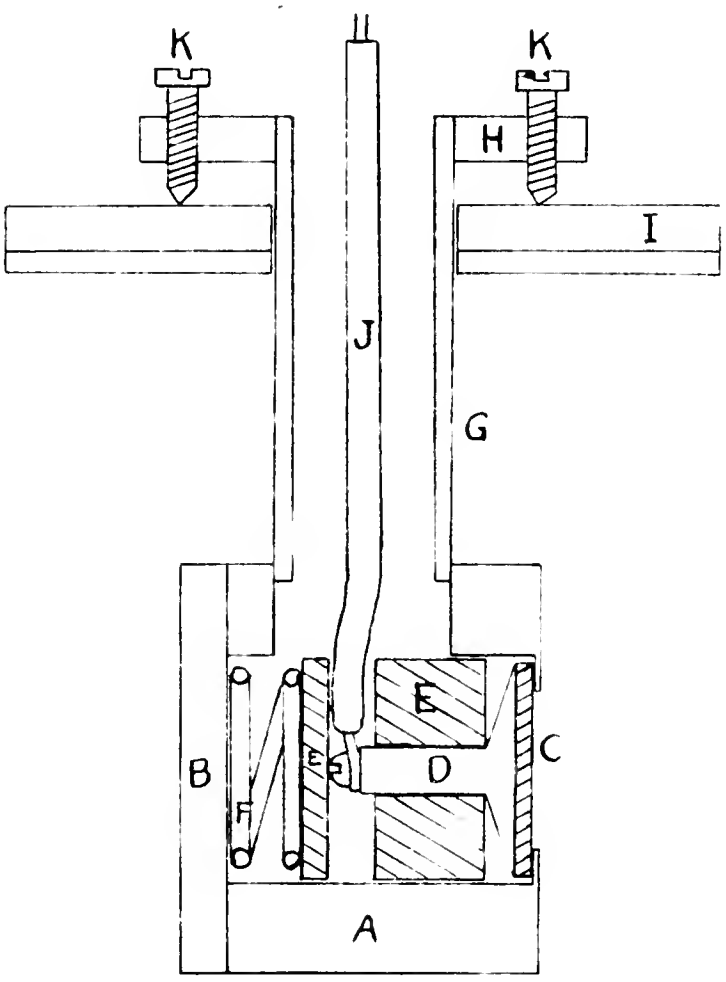
General Arrangement of Apparatus used to Investigate the Dispersion of Sound Velocity in Methyl and Ethyl Acetate

of brass plate. The inside dimensions were as follows: depth, 7 centimeters; width, 4 centimeters; and length, 20 centimeters. The usual liquid sample was about 300 cubic centimeters.

The quartz crystals were mounted in brass holders, which were suspended in the liquid from brass plates mounted on top of the tank. The crystals used were x-cut quartz and were circular in shape with a diameter of 0.75 inches. The resonant frequency of the crystals was 7.0 megacycles with an accuracy of five per cent. Both faces of the crystals were silver-plated to insure good electrical contacts. A detailed cross-section sketch of a crystal holder is shown in Figure 3. The lower part of the holder was made from a brass block (A) by drilling a 0.625 inch hole all the way through the block and then drilling out a 0.825 inch hole from the rear, leaving a small shoulder, 0.01 inches thick, at the face of the block. A brass back plate (B) closed the rear of the block, being fastened to the block by four brass screws. The crystal (C) was then inserted from the rear and fitted against the shoulder of the block. This contact with the crystal served as the electrical ground connection. The electrical potential was applied to the rear face of the crystal by means of a brass disc (D) which was turned down to a small cylinder on the rear side. The electrical connection was then made to this cylinder. The disc was polished on the side toward the crystal and the back side was bevelled, leaving an air space behind the crystal. This air space was necessary to reduce back reflections which gave double and side peaks of

Figure 3

Holder for Quartz Crystal



A Brass Holder Block
B Brass Holder Back Plate
C Quartz Crystal
D Brass Crystal Back Plate
E Bakelite Insulators
F Coil Spring
G Brass Tube
H Brass Shoulder
I Brass Plate to fit on Tank
J Electrical Lead
K Leveling Screws

output current instead of the single peak at the standing wave pattern. Bakelite insulators (E) were inserted to prevent grounding and to keep the crystal centered in the block. In order to hold the crystal snug against the shoulder of the holder two turns of a light coil spring (F) were inserted between the rear insulator and the holder back plate. Some difficulty was encountered in making the holders leak-proof because none of the usual cements or greases could be used due to the solvent properties of the acetates, and also because strong pressure could not be exerted by the spring in the holder due to the danger of distorting the crystal oscillations. This trouble was eliminated by inserting several soft lead foil washers between the crystal and the shoulder of the holder and by not keeping the holders in the liquid any longer than was necessary.

A brass tube (G) was silver-soldered into a hole in the top of the holder block and the electrical connection (J) was introduced through it. This tube was then inserted through a hole in a brass plate (I) which fastened on the top of the liquid tank. At the top of the tube a brass shoulder (H) was mounted to the tube and leveling screws (K) were threaded in the shoulder which bore on the brass plate (I). One of the most critical adjustments in the use of this apparatus was in maintaining the crystal faces parallel and directly opposite to each other. By an adjustment of these leveling screws and with a set of horizontal screws providing horizontal motion, the crystal face could be moved in any direction until parallelism was achieved.

The condition when the faces were not parallel was observable by the fact that the output current was greatly reduced and the minima and maxima of the output current as the frequency was changed became very distorted.

The distance between the crystals was maintained at ten centimeters for all the experimental work, a check being made for correct spacing before and after each set of readings. This distance seemed to be quite satisfactory.

The oscillator was of the standard Hartley type, employing a type 807 transmitter tube. Frequencies between two and five megacycles were obtained by the use of two coils which were changeable and a variable condenser. The complete wiring diagram of the oscillator is attached as Figure 4.

To provide for amplification of the signals from the receiving crystal, a standard type wide band video preamplifier and amplifier was employed. The one used in this work utilized 6AC7 amplifier tubes, providing six stages of amplification. Further amplification was obtained by using a square-law vacuum tube voltmeter. The wiring diagram of the one used in this case is shown in figure 5. The great advantage of this instrument was to increase the sharpness of the peaks of the output current at the frequencies corresponding to standing waves between the crystals. This made possible a much more accurate setting of the oscillator at these frequencies. The output current of the voltmeter was measured on the 100 microampere scale of a Simpson Model 260 meter.

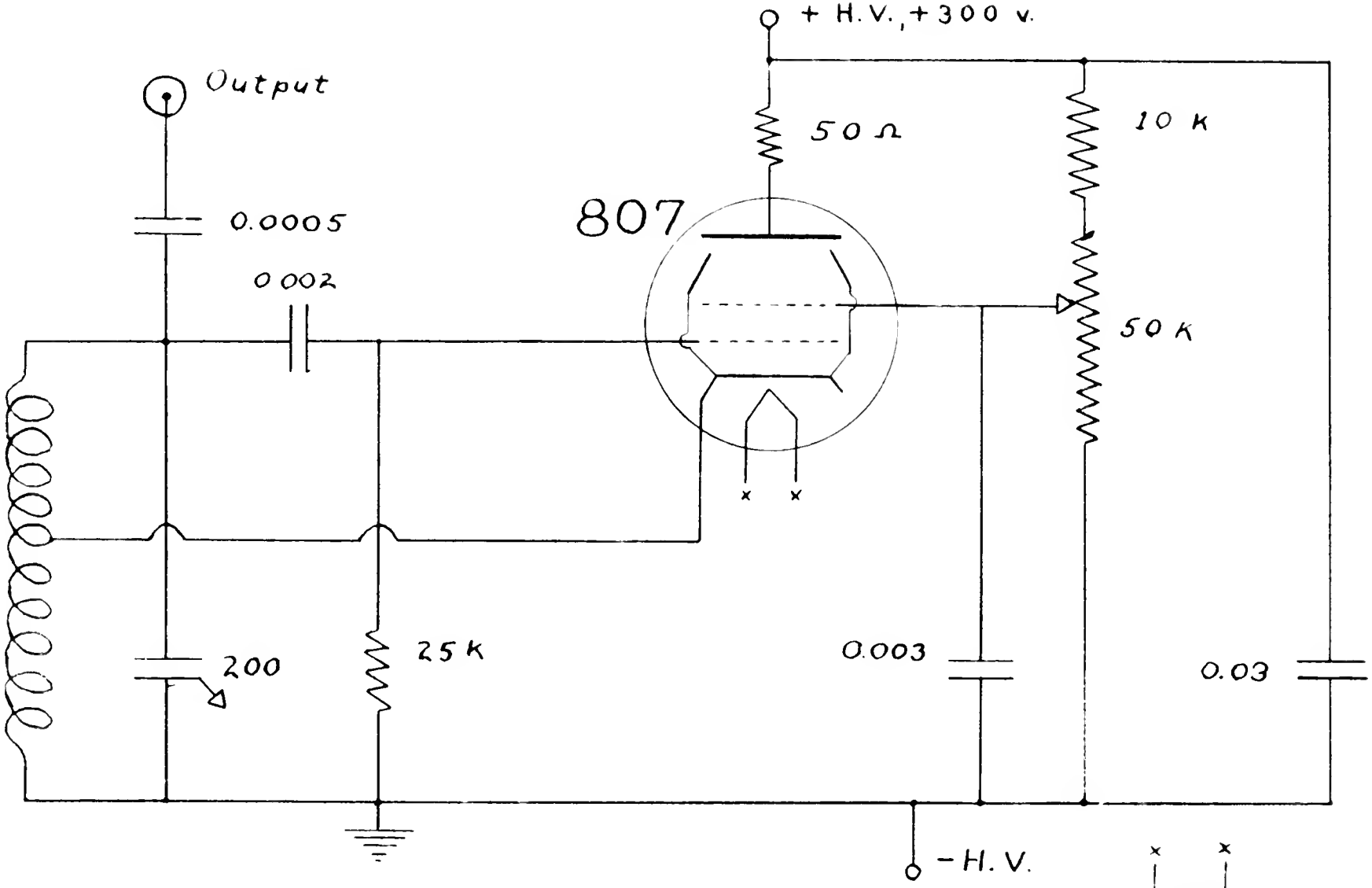


Figure 4

Variable High Frequency Oscillator

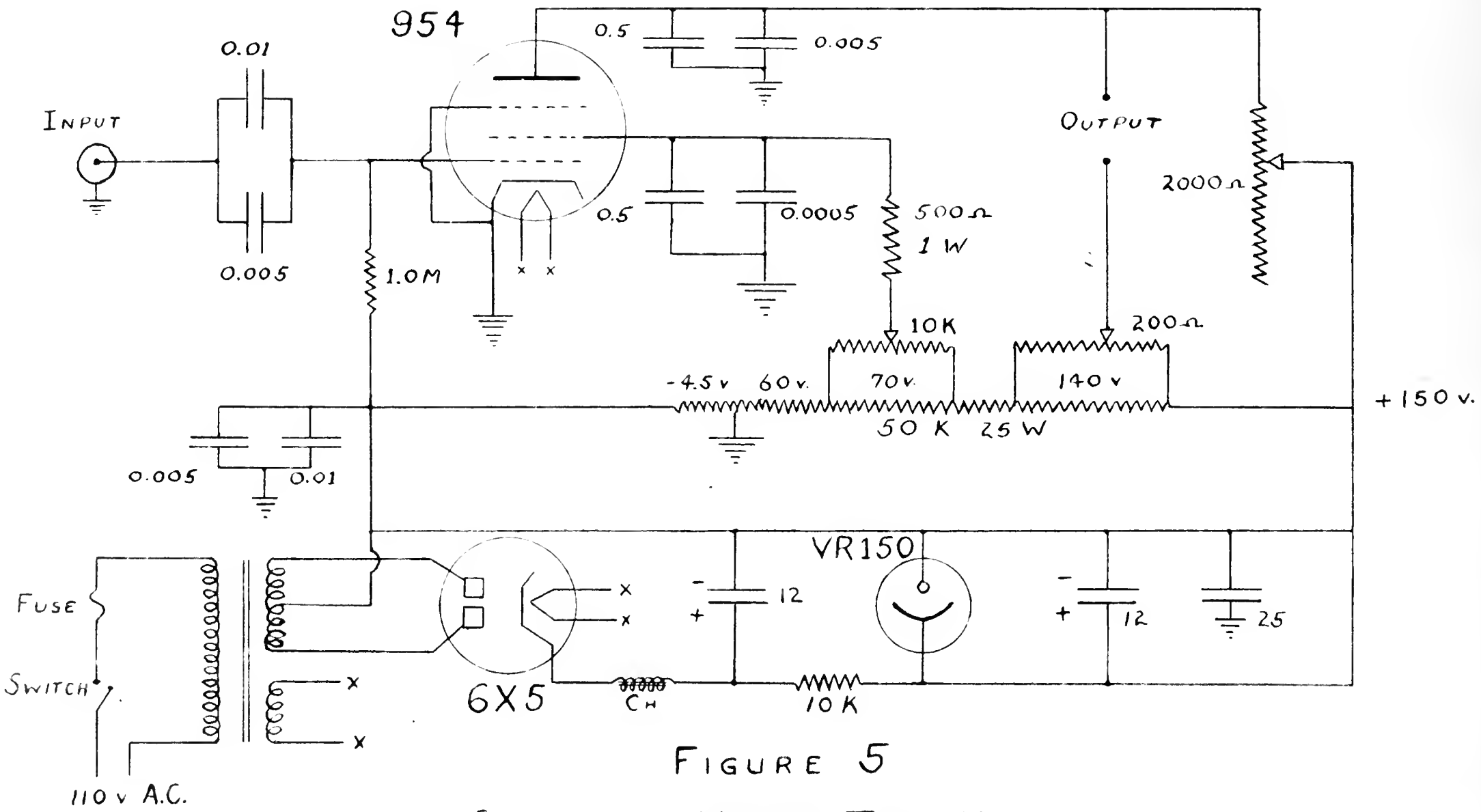
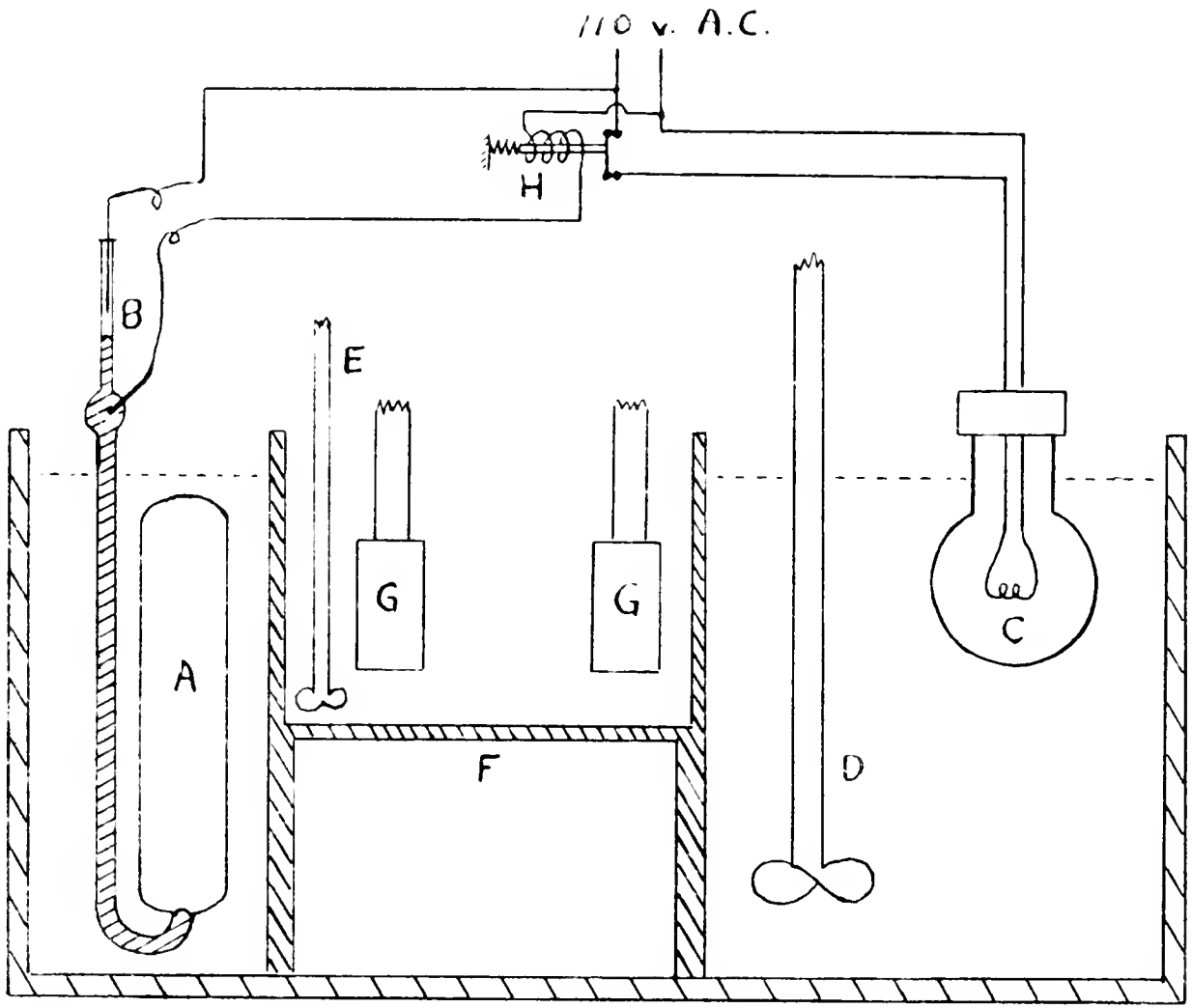


FIGURE 5

SQUARE-LAW VACUUM TUBE VOLTMETER

The velocity of sound is a function of the temperature of the medium in which it is measured. For example, the sound velocity in water changes from 1441 meters/second at 13°C. to 1505 meters/second at 31°C. This represents an increase of about 5 meters/second/degree C. And since the desired accuracy of the results was 0.1% or better, it was necessary to maintain the temperature of the liquid constant to within 0.1°C. for all measurements. To accomplish this, the liquid tank was immersed in a water bath which was kept at 25° ± 0.05°C. The arrangement of the temperature control system is shown in Figure 6. The thermostat was of the liquid expansion type and employed a glass bulb filled with toluene. Mercury was placed above the toluene and provided electrical contact between two electrodes. These electrodes were connected to a relay which controlled the heater. By the expansion or the contraction of the toluene due to a temperature change in the water, contact between the electrodes was established or broken. The water was kept in constant motion by means of a stirrer. As a further precaution against temperature differentials in the liquid sample caused by wave propagation or local density variations, a stirrer was mounted in the cell in order to keep the liquid in circulation. This method of temperature control was sufficient to keep the temperature of the liquid well within prescribed limits.

The biggest problem in this method of measurement proved to be a sufficiently accurate measurement of the frequency increment



A Thermostat Bulb filled with Toluene
B Mercury Filled Capillary showing Electrode Arrangement
C Light Bulb Heater
D Water Bath Stirrer
E Liquid Sample Stirrer
F Liquid Sample Tank
G Crystal Holders
H Normally Closed Relay

Figure 6

Arrangement of Apparatus in Constant Temperature Water Bath

resulting from changing the number of half waves between the crystals by the desired number. Two methods were used (hereafter designated A and B) and the apparatus used in each method is as follows:

(A) A U.S. Army Signal Corps BC 221-P Frequency Meter manufactured by the Zenith Radio Corporation was used to measure the oscillator frequency at which the crystal was being driven. The frequency increment was then obtained as the difference of two measured frequencies.

(B) In the second method the frequency increment was not found from the difference of two measured frequencies but was measured directly. The frequency meter was used as a standard oscillator and the outputs of the crystal oscillator and the frequency meter were used as inputs in a mixer-detector circuit, employing a 6SA7 Tube. The beat frequency of the mixer represented the difference between the frequencies of the two oscillators. This beat frequency was measured by a General Radio Type 224 Precision Wave Meter. A wiring diagram of this mixer arrangement appears in Figure 7. The detailed experimental procedure in each of these methods was the following:

METHOD A - In order to insure stable operation the oscillator, amplifier, and meters were switched on at least two hours before use. After the holders were mounted in the cell and the distance between the crystals was checked, the liquid was placed in the cell and brought to a constant temperature in the water bath. The oscillator was then set at a frequency

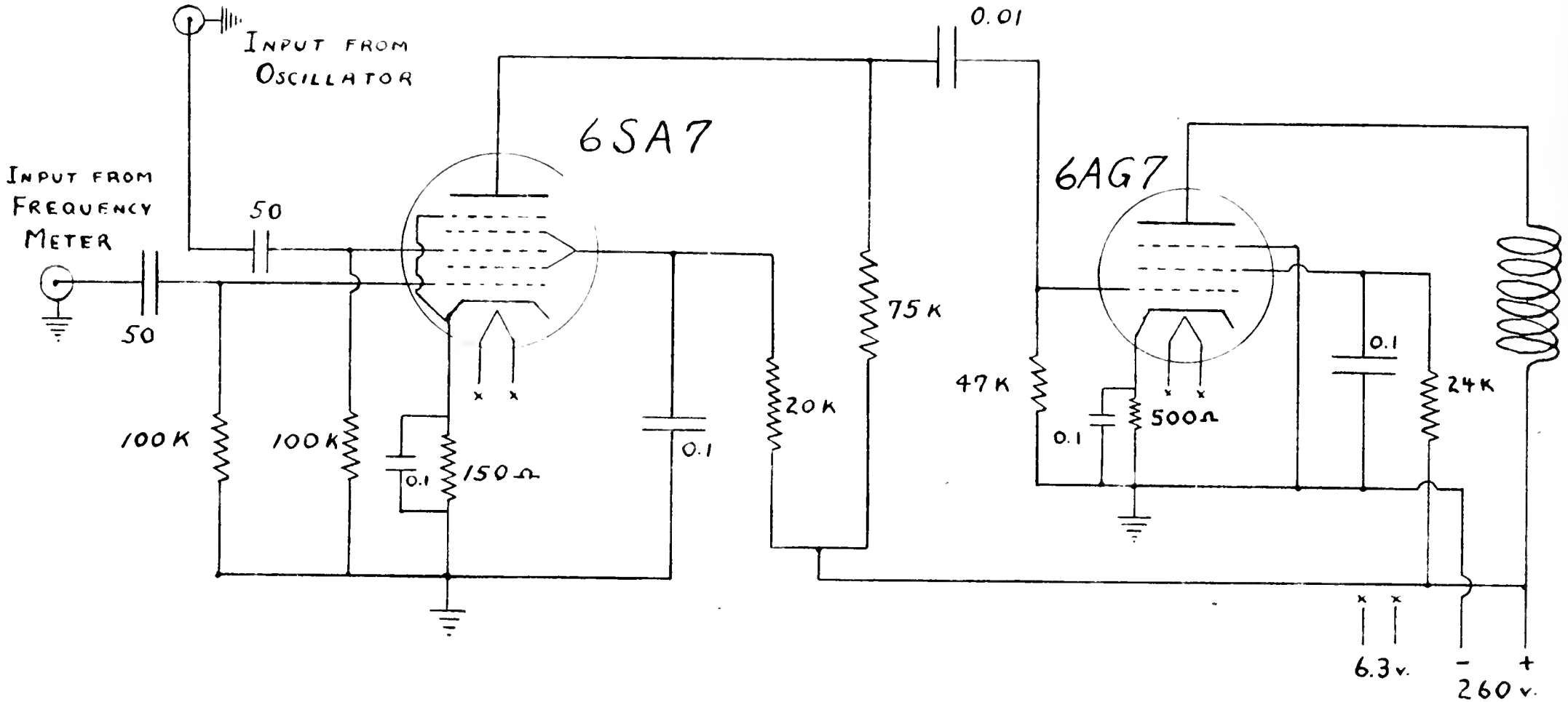


FIGURE 7

MIXER CIRCUIT TO OBTAIN FREQUENCY INCREMENT

at which a standing wave formed between the crystals as indicated by a maximum current at the output meter. After measuring this frequency with the frequency meter, the oscillator frequency was changed until the number of waves between the crystals had been changed by a set increment (as indicated by the number of peaks of the output current). This increment was chosen as eighteen for these measurements, being small enough to be less than 5% of the oscillator frequency and large enough to keep any error in the setting of the oscillator on the peak of the output current sufficiently small. Upon setting on the peak output current again, the frequency was measured with the frequency meter. The frequency increment was then obtained as the difference of the two measured frequencies. The ensuing procedure was to return to the standing wave condition adjacent to that of the initial measurement taken previously and to take another set of readings. This gave, as a check, two increments at approximately the same frequency but on different standing wave conditions. Sets of readings were taken every 0.1 to 0.2 megacycles over the range from two to five megacycles. This method was discarded because of insufficient accuracy, as will be discussed later.

METHOD B - The apparatus was connected as described above under (B), and the following procedure was adopted. Preliminary operations were the same as under Method A, but

the frequency increment was determined differently. As before, the oscillator was set on a frequency of peak output current. The frequency meter was then set at this same frequency, by obtaining zero frequency beat as observed by the mixer detector. After changing the oscillator frequency by the amount which gave the proper increment in the number of half waves between the two crystals, the oscillator was again set on the peak of the output current. Then the difference of the oscillator frequency and the unchanged frequency meter frequency was measured as the beat frequency by the precision wave meter. In this method the increment of half waves was taken as twenty for the acetates and sixteen for the water, since this gave an increment of frequency which was most accurately determined by the wave meter, as will be explained in a discussion of the results.

Measurements were carried out on three liquids: (1) distilled water, which shows no dispersion and which was used to check for proper accuracy; (2) methyl acetate, C.P. Grade, manufactured by Eimer and Amend; and (3) ethyl acetate, C.P. Grade, manufactured by General Chemical Co. These liquids were not redistilled but were used as received from the manufacturer. However, because of contamination and decomposition dangers, each sample was not used for more than two sets of measurements.

III. EXPERIMENTAL RESULTS

At first, measurements were made by Method A described in the previous section. This was the method of finding the frequency increment in terms of the difference of the two frequencies measured on the frequency meter. No check was made on the calibration of the frequency meter and the calibration supplied with the instrument was used. The standing wave increment of eighteen was chosen as being satisfactory. This gave a frequency increment of about one hundred kilocycles which was small enough to be less than five per cent of the total frequency and large enough to make the errors in placing the oscillator at the peak output current relatively small.

A great many measurements were taken by this method in order to obtain proper alignment and functioning of the apparatus. Distilled water was used for the first measurements since all work performed to date indicates that water shows no dispersion. Thus, the accuracy of the method could be checked over the entire frequency range by obtaining a constant frequency increment within the desired accuracy. The desired accuracy, as mentioned earlier, was 0.1% or better. Some results of these measurements on water are shown in Table I under Columns 1, 2, and 3. Each column represents a series of measurements taken without disturbing the adjustments or the condition of the apparatus. Adjustments were made between runs in an attempt to improve the accuracy. These included adjusting the crystals to maximum parallelism, using baffles and

VII. Summary and Conclusions

absorbers to check for any wall effects, changing the oscillating output amplitude, and changing the output amplification. It can be seen in Table 1 that the measured frequency increments are far from constant within the desired accuracy, and that the adjustments mentioned above caused no apparent improvement. The measurements taken at any one frequency agree quite well but the dispersion between the results at different frequencies is considerable. Columns 4 and 5 represent some measurements on methyl acetate by this same method and show about the same amount of random dispersion. After checking all other possible causes, the trouble was attributed to the frequency meter. The calibration was not accurate enough over the entire frequency range to allow the small increment to be determined by the difference of the two large measured frequencies. Another difficulty, the apparent inaccuracy of the frequency meter condensers, was indicated by the inability to reproduce a given measurement.

With this difficulty in mind, the method described as B in the previous section was devised. This was not dependent on an accurate measurement of frequency by the frequency meter. The only requirements on the frequency meter were (1) that it could be used as a standard oscillator, (2) that it could be set accurately at the same frequency as the crystal oscillator, and (3) that it would remain at this frequency for the duration of each measurement. The wave meter was then used to measure the frequency increment as the beat frequency of the mixer after the oscillator was changed

TABLE I

Typical Data Taken By Method A Using $\Delta n = 18$

Frequency (megacycles)	Frequency Increment (kilocycles)				
	Water			Methyl Acetate	
	1	2	3	4	5
2.20	135.09	134.95	135.38	105.19	105.20
2.35				105.66	105.45
2.50	135.41	135.55	135.30	105.37	105.44
2.75	136.12	136.30	136.21	105.64	105.72
3.00	135.23	135.00	135.32	105.41	105.63
3.20	135.32	135.14	135.37	105.33	105.31
3.35				105.32	
3.50	135.59	135.46	134.95	105.46	105.38
3.75	135.29	135.22	135.18	105.80	105.08
4.05				104.39	104.50
4.30	135.13	135.09	135.09	105.27	105.09
4.50	135.67	135.50	135.63	105.34	105.05
4.65	135.67	135.54		105.24	105.95
5.00	135.47	135.32		105.00	105.37

through the half wave increment. The improved results of this method are shown in Table II for water between 2.0 and 4.8 megacycles. Here the increment of half waves was chosen as twenty since this gave a frequency increment measurable to maximum accuracy on the wave meter. With this increment, the conversion of the wave meter scale reading to frequency was almost linear and the number of kilocycles per wave meter scale division was a minimum. It may also be noted that this method is independent of an exact calibration of the wave meter and depends only on its stability and the ease of observing small increments of frequency. Since the frequency increment is always approximately the same, only small deviations from the same wave meter setting are recorded; the absolute value of the increment does not need to be known very precisely. The results shown for water were much more satisfactory than those previously obtained, the average frequency increment being 120.00 kilocycles with an average error of only 0.07 kilocycles. The total dispersion between the largest and the smallest result was only 0.27 kilocycles.

Thus, with the desired accuracy obtained, measurements were taken on the acetates. The results of the methyl acetate measurements are shown in Table III and those for ethyl acetate in Table IV. In these measurements, the half wave increment was chosen as sixteen in order that the same region of maximum accuracy of the wave meter could be utilized which was described in the previous paragraph. Each result in the tables represents the average value of several measurements (seven or more) of the frequency increment.

TABLE II

Measurements on Water Using Method 3 with $\Delta n = 16$ Confirming No Dispersion and Indicating an Apparatus Error of Less Than 0.1 %.

Frequency (megacycles)	Frequency Increment (kilocycles)	Deviation
2.0	119.95	- 0.05
2.2	120.00	- 0.00
2.35	119.95	- 0.05
2.45	119.88	- 0.12
2.55	119.90	- 0.10
2.70	119.93	- 0.07
2.75	119.95	- 0.05
2.95	119.98	- 0.02
3.10	120.02	+ 0.02
3.15	120.00	0.00
3.25	120.10	+ 0.10
3.40	119.94	- 0.06
3.60	120.15	+ 0.15
3.70	119.90	- 0.10
3.90	120.06	+ 0.06
4.0	120.03	+ 0.03
4.15	120.10	+ 0.10
4.25	120.09	+ 0.09
4.45	120.07	+ 0.07
4.6	120.00	0.00
4.8	120.07	+ 0.07

Average Value = 120.00 ± .07 Kilocycles

TABLE III

Summary of Results for Methyl Acetate

Method B $\Delta n = 20$ $T = 25^\circ$ C.

Frequency (megacycles)	Frequency increment (kilocycles)	Frequency (megacycles)	Frequency increment (kilocycles)
2.003	116.13 ± .04	2.015	116.15 ± .07
2.095	116.16 ± .08	2.107	116.13 ± .07
2.200	116.14 ± .04	2.211	116.14 ± .08
2.303	116.14 ± .05	2.315	116.16 ± .06
2.407	116.22 ± .06	2.419	116.16 ± .06
2.598	116.18 ± .05	2.609	116.13 ± .02
2.702	116.10 ± .03	2.713	116.09 ± .04
2.819	116.13 ± .09	2.824	116.09 ± .04
2.909	116.09 ± .04	2.921	116.08 ± .05
3.001	116.12 ± .05	3.006	116.10 ± .04
3.153	116.14 ± .06	3.163	116.07 ± .05
3.200	116.05 ± .03		
3.245	116.07 ± .06	3.290	116.16 ± .09
3.303	116.12 ± .05	3.305	116.10 ± .04
3.336	116.21 ± .09	3.304	116.14 ± .06
3.408	116.10 ± .05	3.413	116.10 ± .05
3.449	116.14 ± .04	3.454	116.10 ± .03
3.500	116.17 ± .08		
3.599	116.07 ± .05	3.604	116.12 ± .10
3.700	116.16 ± .12	3.705	116.14 ± .06
3.800	116.13 ± .04	3.805	116.12 ± .09

TABLE III

(Continued)

4.002	116.11 ± .08	4.008	116.03 ± .03
4.094	116.06 ± .09	4.100	116.11 ± .09
4.298	116.21 ± .03	4.302	116.15 ± .09
4.400	116.15 ± .09	4.406	116.14 ± .06
4.602	116.15 ± .05	4.608	116.14 ± .06
4.850	116.10 ± .06		

Average increment = 116.12 kilocycles

Average error = ± 0.06 kilocycles

TABLE IV

Summary of Results for Ethyl Acetate

Method B $\Delta n = 20$ $T = 25^{\circ}C.$

Frequency (megacycles)	Frequency Increment (kilocycles)	Frequency (megacycles)	Frequency Increment (kilocycles)
2.003	114.67 ± .08	2.009	114.68 ± .06
2.095	114.64 ± .05	2.101	114.65 ± .05
2.197	114.67 ± .06	2.208	114.72 ± .07
2.300	114.69 ± .06	2.312	114.66 ± .03
2.402	114.83 ± .08	2.414	114.82 ± .06
2.494	114.71 ± .06	2.506	114.69 ± .06
2.596	114.81 ± .06	2.608	114.76 ± .06
2.702	114.69 ± .06	2.712	114.68 ± .06
2.818	114.75 ± .04	2.827	114.69 ± .04
2.906	114.68 ± .05	2.911	114.80 ± .03
2.957	114.67 ± .02	3.009	114.71 ± .05
3.157	114.77 ± .04	3.169	114.73 ± .05
3.226	114.71 ± .02	3.231	114.77 ± .05
3.316	114.79 ± .03	3.322	114.71 ± .02
3.402	114.75 ± .05	3.408	114.73 ± .03
3.499	114.65 ± .03	3.504	114.65 ± .06
3.591	114.68 ± .04	3.597	114.64 ± .02
3.699	114.71 ± .02	3.709	114.69 ± .06
3.853	114.69 ± .05	3.858	114.61 ± .04
4.084	114.81 ± .02	4.190	114.73 ± .05
4.283	114.7[illegible] ± .03	4.294	114.76 ± .03

TABLE IV

(Continued)

4.406	114.75 ± .05	4.422	114.75 ± .03
4.594	114.70 ± .03	4.600	114.72 ± .05
4.716	114.64 ± .08	4.722	114.64 ± .04

Average increment = 114.71 Kilocycles

Average error = ±0.05 Kilocycles

The frequencies, it is noted, occur in pairs very close together in most cases and they represent increments taken from frequencies one or two standing wave peaks apart. The error represents the average error of each increment, and was determined as follows: the deviations of all measurements at one frequency from the average value of these measurements were squared and the squared deviations were summed. This sum was divided by the number of measurements and the square root was taken. This was the average error. The measurements at any one frequency from which the values in the tables were computed were not taken at one time but they represent at least two different runs in all cases.

To give a better assessment of these results, the figures shown in Tables III and IV are shown plotted on Figure 8. Where two results were obtained at closely adjoining frequencies, both results were plotted at a frequency about midway between the two experimental frequencies. Thus, at any one plotted frequency, four increment values are plotted - the maximum and minimum average increment values found at the frequency just below the plotted one and the maximum and minimum values at the frequency just above the plotted one. Small horizontal marks are used to indicate these values and to indicate to which set each value belongs.

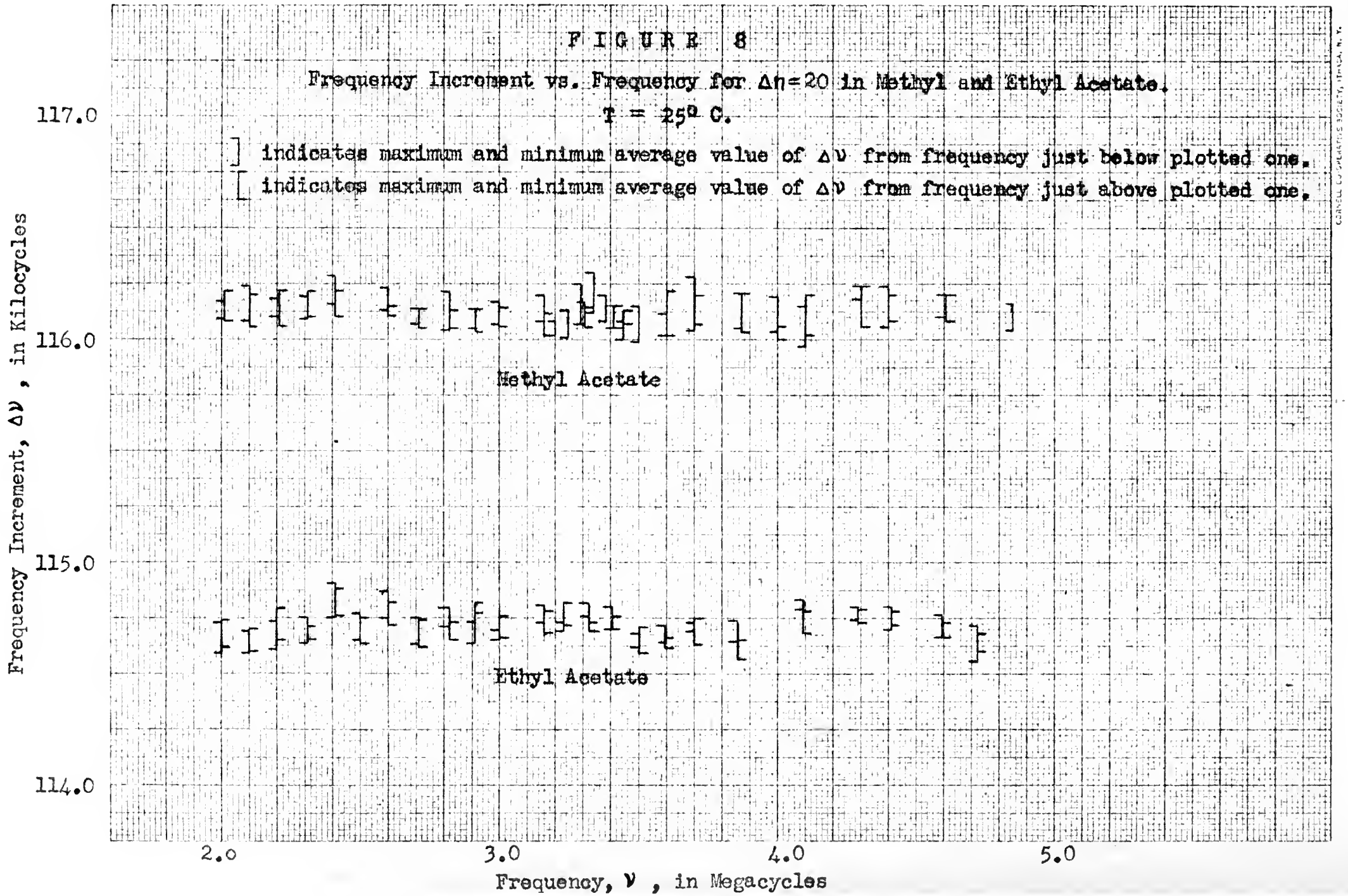


FIGURE 8
Frequency Increment vs. Frequency for Δη=20 in Methyl and Ethyl Acetate.
T = 25° C.
] indicates maximum and minimum average value of Δν from frequency just below plotted one.
[indicates maximum and minimum average value of Δν from frequency just above plotted one.
117.0
116.0
115.0
114.0
Frequency Increment, Δν , in Kilocycles
Methyl Acetate
Ethyl Acetate
2.0
3.0
4.0
5.0
Frequency, ν , in Megacycles

IV. CONCLUSIONS

In their work on the absorption of ultrasonics in liquids, Claeys, Errera, and Sack reported anomalous absorption by methyl and ethyl acetate in the frequency region between three and four megacycles. The variation of the absorption coefficient was quite similar to that obtained in polyatomic gases. The experimental results for the gases were explained by the Kneser theory using a relaxation time for the intramolecular energy exchanges. Such an explanation, if applicable to liquids, should also lead to a dispersion of velocity in the anomalous absorption frequency region. The results of the experimental work reported in Tables III and IV and on Figure 8 of the previous section indicate that there is no dispersion of the sound velocity in this frequency region, at least not within the accuracy of the apparatus. The velocity dispersion predicted by the Kneser theory is such that the velocity increases slowly in the anomalous absorption region. This would have yielded an increasing frequency increment over the frequency range under investigation. No such result as this was obtained experimentally.

This failure to obtain any velocity dispersion may be interpreted in either of two ways, assuming that these acetates do show the reported anomalous absorption behavior at the frequencies under investigation. First, the dispersion may still be present but may be too small to be detected by the experimental method which was used. This is possible since, as was pointed out earlier, any

IV. [illegible]

velocity dispersion will be small because in the case of liquids the specific heat due to the vibrations of the molecules is a much smaller part of the total specific heat than in gases. It was further estimated in the introduction that any dispersion due to a relaxation time process would be of the order of 0.05% which was about the limit of accuracy of the measurements. A second possible interpretation of the results is that the anomalous absorption is due to some phenomenon which does not cause a velocity dispersion at the same time. Such processes are among the many theories which have been proposed to account for the abnormal absorption of liquids but as yet none of these have been completely acceptable.

However, from the experimental results of this work, no conclusions may be drawn as to the explanation of the abnormal absorption of these liquids. It is only possible to say that it appears that there is no dispersion of velocity in the frequency range from two to five megacycles, or that any dispersion which does exist is less than 0.06%.

While the experiment was not designed to measure the absolute sound velocity, it is possible to calculate the velocity, if it does not change with the frequency, by rearranging the equation derived in Section II as follows:

$$V = \frac{\Delta\nu}{\Delta n} 2d$$

where $\Delta\nu$ is the frequency increment in cycles/second, d is the distance between the crystals in meters, Δn is the half

$$V = \frac{\Delta n}{\Delta p} \, \epsilon \, d$$

wave increment, and V is the velocity of sound in meters/second. In all the results given, d was 0.10 meters. In Table II the results for water were: $\Delta\nu$ = 120.00 kilocycles and Δn = 16. In Table III the results for methyl acetate were: average $\Delta\nu$ = 116.12 kilocycles and Δn = 20. In Table IV the results for ethyl acetate were: average $\Delta\nu$ = 114.71 kilocycles and Δn = 20. Using these values the following values for the velocity of sound at 25°C were obtained: water, 1500 meters/second; methyl acetate, 1161.2 meters/second; and ethyl acetate, 1147.1 meters/second.

To summarize the principle conclusions, no dispersion of sound velocity in methyl acetate or ethyl acetate was found as the frequency of the sound waves is varied from two to five megacycles within the experimental error of about 0.06%. The failure to locate any dispersion in this frequency region where anomalous absorption has been reported for these liquids may be due to the fact that the dispersion is smaller than the accuracy of the measurements or that the anomalous absorption is caused by a process not producing velocity dispersion. With only this information it is not possible to draw any conclusions concerning the existence of any relaxation time phenomenon in this frequency region.

V. BIBLIOGRAPHY

1. G. G. Stokes, Trans. Camb. Phil. Soc. 8, 297 (1845). Phil. Mag. 1, 305 (1851).
2. G. Kirchhoff, Pogg. Ann. 134, 177 (1868).
3. G. W. Pierce, Proc. Am. Acad. Sci. 63, 1 (1928).
4. H. O. Kneser, Ann. d. Physik 11, 761, 777 (1931).
5. N. Nekolepajew, Ann. d. Physik 35, 175 (1911).
6. D. L. Rich and W. H. Pielmeyer, Phys. Rev. 25, 117 (1925).
7. E. Grossman, Ann. d. Physik 13, 681 (1932); Physik. Zeits. 33, 202 (1932).
8. T. P. Abello, Proc. Nat. Acad. Sci. 13, 699 (1927); Phys. Rev. 31, 1083 (1928).
9. A. Einstein, Sitz. Berl. Akad., 380 (1920).
10. Sir James Jeans, Dynamical Theory of Gases, (Cambridge University Press, 1904 Edition).
11. K. Herzfeld and F. O. Rice, Phys. Rev. 31, 691 (1928).
12. A. J. Rutgers, Ann. d. Physik 16, 350 (1933).
13. D. G. Bourgin, Nature Lond. 122, 133 (1928); Phil. Mag. 7, 821 (1929); Phys. Rev. 34, 521 (1929); 42, 721 (1932); 50, 355 (1936); J. Acoust. Soc. Amer. 4, 108 (1932); 5, 57 (1934).
14. E. Biquard, Comptes rendus 188, 1230 (1929); 202, 117 (1936); Ann. d. Physique 6, 195 (1936).
15. Ch. Sörensen, Ann. Phys. Lpz. (V) 26, 121 (1936).

Bibliography

16. J. Claeys, J. Errera, and H. Sack, Comptes rendus 202, 1493 (1936); Trans. Faraday Soc. 33, 136 (1937).

17. R. Lucas, Comptes rendus 201, 1172 (1935); 203, 459 (1936); 203, 611 (1936); J. de Phys. et rad. 8, 41 (1937).

18. P. Bazulin, Physik Zeits. Sowjetunion 8, 354 (1935); Comptes rendus, USSR 3, 285 (1936).

19. A. Bär, Helv. Phys. Acta 10, 332 (1937).

20. E. Riedemann, N. Seifen, and E. Schreur, Naturwiss. 24, 681 (1936).

21. S. Parthasarathy, Proc. Ind. Acad. Sci. 4A, 222 (1936).

22. D. J. Spakovskij, Comptes rendus, USSR 18, 169 (1938).

23. Willard, J. Acoust. Soc. Amer. 12, 438 (1941).

24. W. T. Richards, Rev. Mod. Phys. 11, 34 (1939).

25. K. S. Krishnan, Pro. Ind. Acad. Sci. A 13, 281 (1941).

26. Pinkerton, Nature Lond. 162, 106 (1948).

27. S. Parthasarathy, Curr. Sci. 6, 501 (1938).

28. R. Boyer and R. Smith, J. Acoust. Soc. Amer. 18, 424 (1946).

29. G. W. Pierce, Proc. Am. Acad. Sci. 63, 1 (1928).

30. P. Debye and F. Sears, Proc. Nat. Acad. Sci. 8, 409 (1932).

31. R. Lucas and P. Biquard, Comptes rendus 194, 2132 (1932).

DATE DUE			

Thesis 11659
E4 Ellis
The dispersion of the
velocity of sound in
methyle and ethyl acetate.